



Durable flame retardant finishing of the nylon/cotton blend fabric using a hydroxyl-functional organophosphorus oligomer

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Abstract

Cotton/nylon blends have been commonly used as the material for protective clothing, but those blend fabrics are not flame retardant finished because of the unavailability of effective flame retardant finishing systems. Previously, we investigated the use of a hydroxyl-functional flame retardant organophosphorus oligomer (FR) in combination with the mixture of dimethyloldihydroxyethyleneurea (DMDHEU) and trimethylolmelamine (TMM) as the binders for flame retardant finishing of cotton. In this study, we investigated the application of FR to the 50/50 cotton/nylon fabric. When the FR/DMDHEU/TMM system is applied to the fabrics of nylon-6,6 and nylon-6, approximately 40% of the FR applied is permanently bound to the nylon fabrics. FR is bound to the nylon fabrics mainly through the formation of a FR/TMM crosslinked polymeric network, thus becoming durable to multiple launderings. The cotton/nylon blend treated with FR shows high levels of flame retardant performance and excellent laundering durability. The treated fabric passes the vertical flammability test even after 50 home laundering cycles. The fabric stiffness as a result of the finishing process is still an obstacle to be overcome for practical use of this finishing system.

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1. Introduction

It is difficult to impart durable flame retardancy to nylon fabrics due to low reactivity of nylon and poor penetration of a finishing solution into the fibers. Although aramid fibers, such as Nomex and Kelvar, are inherently flame resistant, the high cost of those aramide fibers has limited their wide applications. In recent years, flame retardant finishing of nylon and nylon/cotton blend fabrics has drawn more and more attention because those fabrics are widely used to

produce protective clothing for military as well as civilian uses.

Several review articles on flame retardant nylon have been published [1–5]. Flame retardant nylon fibers can be produced at the fiber spinning stage using flame retardant additives including organophosphorus and halogenated aliphatic/aromatic compounds [1–4]. However, the high level of the additives required to achieve the flame retardancy may cause significant strength loss of the fiber, and technical difficulties are often encountered during the spinning procedure [1,3]. The second approach is flame retardant finishing of nylon fabrics using a pad-dry-cure process. A number of flame retardant finishing systems, such as thiourea derivatives, ammonium sulfamate and organophosphorus compounds, have been reported as the flame retardant treatment for nylon fabrics using this method [4–10].

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However, none of those technologies has achieved any substantial commercial success.

The flame retardant finishing of a blend fabric containing cotton and a thermoplastic synthetic fiber is difficult because of the “scaffolding effect” of the blend [2,3]. A number of patents have disclosed the use of phosphorus-containing flame retardant agent including the tetrakis(hydroxymethyl)-phosphonium (THP) and urea precondensate to treat cotton/nylon blend, but those flame retardant finishing systems have not been commercialized [11–16]. The nylon/cotton (50/50) blend twill fabric, known as Battledress Uniform (BDU) fabric used to make military uniforms in the U.S., is currently not flame retardant finished due to the unavailability of effective flame retardant finishing technologies.

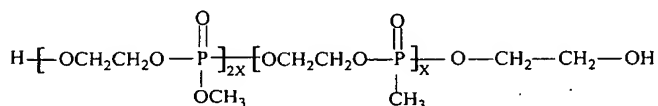
In our previous study, we used the hydroxyl-functional organophosphorus oligomer with the commercial name of “Fyroltex HP” shown in Scheme 1 (CAS Register No. 70715-06-9, abbreviated as “FR” here) as a flame retardant finishing agent for cotton fabrics when DMDHEU, TMM or multifunctional carboxylic acids were used as the binders [17–21]. The cotton fabric treated with the finishing solution containing FR, DMDHEU and TMM showed excellent flame retardant performance even after 50 home laundering cycles [19,20]. In those finishing systems, both DMDHEU and TMM function as the binders between FR and cotton cellulose and also as the nitrogen providers to enhance the flame retarding performance of FR due to phosphorus–nitrogen synergism [19–21].

In this study, we investigated the bonding of FR to the nylon fabrics as well as to the cotton/nylon blend fabric. We evaluated the flame retardant performance and laundering durability of the cotton/nylon BDU fabric treated with FR in combination with a bonding system.

2. Experimental

2.1. Materials

Three fabrics were used in this study: (1) 100% nylon-6 knit fabric (Testfabrics Style 304) weighing 73 g/m²; (2) 100% nylon-6,6 woven fabric (Testfabrics Style 306A) weighing 59 g/m²; and (3) 50/50 nylon/cotton BFU printed fabric weighing 216 g/m². FR (“Fyroltex HP”) was a commercial product with nearly 100% active



Scheme 1. The hydroxy-functional organophosphorus oligomer (FR).

ingredient supplied by Akzo Nobel Phosphorus Chemical Division, Dobbs Ferry, New York. DMDHEU was a commercial product (44% solid content) with the trade name of “Freerez 900” supplied by Noveon, Cleveland, Ohio. Two melamine–formaldehyde resins were used in this study: (1) TMM, a commercial product (80% solid content) with the trade names of “Aerotex M-3” and (2) XMM, a commercial product of melamine–formaldehyde having the functionality of 4–5 (85% solid content) with the trade name of “Aerotex 3730”. Those two melamine–formaldehyde resins were supplied by Noveon, Cleveland, Ohio. The catalyst was an NH₄Cl-based commercial product with the trade name of “Catalyst RD” supplied by Eastern Color & Chemical, Greenville, South Carolina.

2.2. Fabric treatment and home laundering procedures

The fabric was first immersed in a finish solution containing FR, the binding agents and the catalyst, then passed through a laboratory padder with two dips and two nips, dried at 90 °C for 3 min, and finally cured in a Mathis curing oven at a specified temperature. All concentrations presented in this study were based on weight of bath (w/w, %) and concentrations of FR, DMDHEU and TMM in all solutions are based on the solid of the chemicals in those chemical products. The wet pick-up of the cotton/nylon fabric was approximately 75%. The wet pick-up of the nylon-6,6 woven fabric and the nylon-6 knit fabric were approximately 60% and 150%, respectively. After curing, the treated fabric was subjected to a specified number of home laundering washing/drying cycles with the use of “AATCC Standard Detergent 1993”. The home laundering washing/drying process was done according to AATCC Test Method 124-1996 (“Appearance of Fabrics After Repeated Home Laundering”). The water temperature of laundering was approximately 46 °C.

2.3. Evaluation of the flame retarding performance of the fabrics

The vertical flammability of the cotton fabric is measured according to ASTM Standard Method D6413-99. The limiting oxygen index (LOI) of the cotton fabric is measured according to ASTM Standard Method D2863-97.

2.4. Determination of phosphorus concentration on the treated fabric

Approximately 2 g of the treated fabric sample taken from three different parts of a “10 × 12” fabric specimen were ground in a Wiley mill into a powder to improve sample uniformity. Two milliliters of

concentrated H_2SO_4 were added to 0.1 g of the powder in a beaker. Ten milliliters of 30% H_2O_2 were added dropwise to the mixture, allowing the reaction to subside between drops. The reaction mixture was then heated at approximately 250 °C to digest the powder and to evaporate the water until dense SO_3 vapor was produced. The completely digested sample as a clear solution was transferred to a 50 ml volumetric flask, and then diluted with distilled/deionized water. The sample thus prepared was analyzed with a Thermo-Farrell-Ash Model 965 inductively coupled plasma atomic emission spectrometer (ICP/AES) to determine the percent concentration of phosphorus. The percent phosphorus retention is calculated by dividing the phosphorus content of the fabric after laundering by that of the fabric before laundering.

2.5. Thermal analysis

Thermogravimetric (TG) experiments were carried out using a Mettler Toledo TGA 851 thermogravimetric analyzer. Samples weight is in the range of 6–8 mg. All samples for TGA were measured from 50 °C to 800 °C at the heating rate 10 °C/min with a continuous air flow. Differential scanning calorimetry (DSC) was measured using a Mettler Toledo DSC 821 analyzer. Aluminum sample holders were used. All samples for DSC were measured from 50 °C to 650 °C at the heating rate of 10 °C/min with a continuous air flow.

3. Results and discussion

The nylon-6,6 fabric was treated with 40% FR in combination with 2.6% DMDHEU and 4.8% TMM, dried at 90 °C for 3 min, finally cured at 165 °C for 2 min. The fabric thus treated was subjected to three home laundering cycles. The phosphorus concentration on the treated nylon fabric before laundering was 3.63%, and it became 1.52% after one laundering cycle and remained statistically unchanged after three home laundering cycles (Table 1). One observes that 41% of the FR applied to the nylon-6,6 fabric remained on the fabric after three home laundering cycles.

Table 1
Phosphorus content (%) and percent phosphorus retention of the nylon-6,6 fabric treated with 40% FR, 2.6% DMDHEU and 4.8% TMM, cured at 165 °C for 2 min and subjected to different number of laundering cycles

Number of laundering cycles	Phosphorus concentration (%)	Phosphorus retention (%)
0 ^a	3.63	—
1	1.52	42
3	1.50	41

^a Before laundering.

Table 2

Phosphorus content (%) and phosphorus retention of the nylon-6 fabric treated with 40% FR, 2.6% DMDHEU and 4.8% TMM, cured at 165 °C for 2 min and subjected to different number of laundering cycles

Number of laundering cycles	Phosphorus concentration (%)	Phosphorus retention (%)
0	6.51	—
1	2.72	42
3	2.72	42

The nylon-6 fabric was also treated with the same finishing solution and cured at 165 °C for 2 min. The amount of FR applied to the nylon-6 fabric was significantly higher than that applied to the nylon-6,6 fabric as a result of the drastically higher wet pick-up due to the loose structure and higher absorbency of the knit fabric. The initial phosphorus concentration on the treated nylon fabric before laundering was 6.51% (Table 2). After the treated nylon-6 fabric was subjected to three home laundering cycles, however, the percent retention of phosphorus on the nylon-6 fabric (42%) was very close to that on the treated nylon-6,6 fabric (41%). It should also be pointed out that the amount of phosphorus on the treated nylon fabrics shows almost no reduction as the number of home laundering cycles increased from one to three (Tables 1 and 2). Thus, the data presented here clearly indicate that the flame retardant organophosphorus oligomer bound to the nylon fabrics was durable to multiple home laundering cycles.

Thermal analysis techniques (TG, DTG and DSC) were used to study the nylon-6,6 and nylon-6 fabrics treated with the finishing solution containing FR/DMDHEU/TMM described above. The TG, DTG and DCS curves of the treated nylon-6,6 fabric measured in air atmosphere are presented in Figs. 1, 2 and 3, respectively. The untreated nylon-6,6 fabric started to lose weight at 360 °C (Fig. 1). The rate of weight loss reached its maximum at 412 °C as indicated

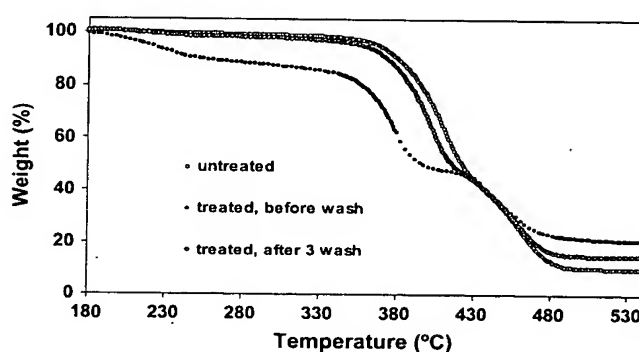


Fig. 1. TG curves of the untreated nylon-6,6 fabric and that treated with 40% FR, 2.6% DMDHEU and 4.8% TMM, and cured at 165 °C for 2 min.

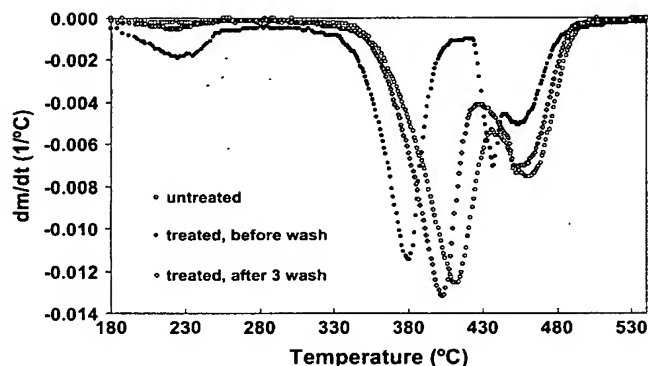


Fig. 2. DTG curves of the untreated nylon-6,6 fabric and that treated with 40% FR, 2.6% DMDHEU and 4.8% TMM, and cured at 165 °C for 2 min.

by the peak in the DTG curve (Fig. 2). The weight loss of the untreated nylon fabric was attributed to the thermal decomposition of nylon-6,6, which caused the main chain breakdown with the formation of NH_3 , H_2O , CO , CO_2 and hydrocarbons [22,23]. The decomposition of nylon-6,6 in this temperature range is confirmed by the endothermal peak at 412 °C in the DSC curve of the nylon-6,6 fabric (Fig. 3). The untreated nylon-6,6 lost 90% of its original weight with 10% residual solid at 500 °C (Fig. 1).

After the nylon-6,6 fabric was treated with FR and before it underwent home laundering, the rate of weight loss of the fabric thus treated reached its maximum at 379 °C as a result of the presence of FR on the nylon fabric (Fig. 2), and the DSC curve of the fabric also shows an endothermal peak at 379 °C (Fig. 3). The treated fabric lost 79% of its original weight as the temperature was increased to 500 °C with 21% solid residual (Fig. 1). The data presented indicate that the presence of the organophosphorus oligomer on the nylon fabric lowered the decomposition temperature

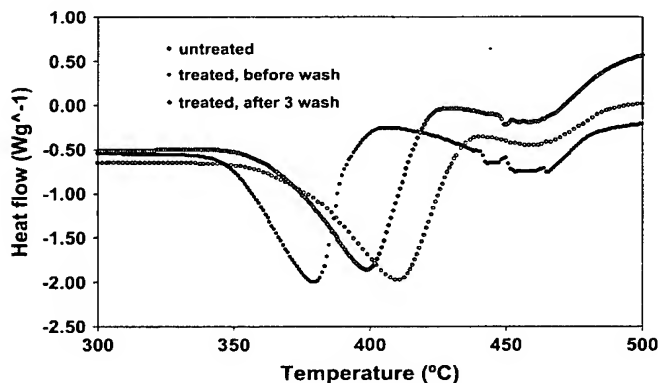


Fig. 3. DSC curves of the untreated nylon-6,6 fabric and that treated with 40% FR, 2.6% DMDHEU and 4.8% TMM, and cured at 165 °C for 2 min.

and enhanced the formation of char after pyrolysis of the fabric sample.

The TG, DTG and DSC curves of the nylon-6,6 fabric treated with FR and subjected to three home laundering cycles are also presented in Figs. 1, 2 and 3, respectively. Both DTG and DSC curves show the decomposition peak at 398 °C, which is notably lower than that of the untreated nylon (412 °C). The TG curve reveals that the nylon-6,6 fabric lost 83% of its original weight at 500 °C with 17% solid residual (Fig. 1). The data presented here clearly suggest that the FR on the treated nylon-6,6 fabric not only lowered the decomposition temperature but also increased quantity of the solid residual after pyrolysis during the TG experiment.

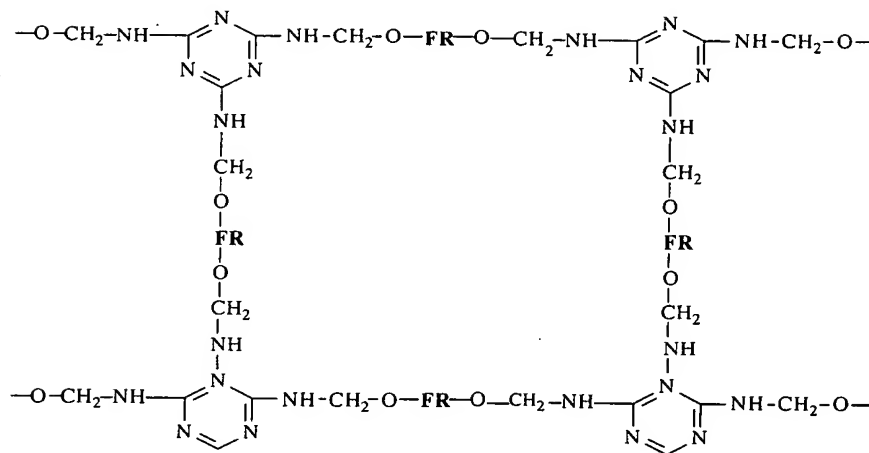
We also studied the effects of the FR-based finishing system on the thermal properties of the nylon-6 fabric using the thermal analysis techniques. The nylon-6 fabric was also treated with the finishing solution containing 40% FR, 2.6% DMDHEU and 4.8% TMM, and cured at 165 °C for 2 min. The TG, DTG and DSC data are summarized in Table 3. One observes similar phenomenon that the decomposition temperature of the treated fabric was reduced and the solid residual after pyrolysis was increased when the nylon-6 fabric was treated with FR/DMDHEU/TMM. Thus, the thermal analysis data of both the treated nylon-6,6 and the treated nylon-6 fabrics demonstrate that the organophosphorus oligomer applied to the nylon fabrics was retained on the fabrics after home laundering.

The fact that more than 40% of the FR applied to the two different nylon fabrics remained on the fabrics after three home laundering cycles demonstrates that the FR applied to the nylon fabric has good laundering durability after the curing process. The bonding of FR to the nylon fiber may be attributed to the reactions of the bonding agents (DMDHEU or TMM) with both FR and terminal amine groups of the nylon fibers. Those bonding agents had multiple hemiacetal groups in their molecules to react with both hydroxyl groups of FR and the terminal amine groups of the nylon fibers, thus forming "bridges" between FR and the nylon fibers. The typical concentration of the terminal amine group of nylon-6,6 is 40 $\mu\text{mol/g}$ [24]. Assuming FR reacts

Table 3

The DTG peaks, DSC peaks and the TG total weight loss of the untreated nylon-6 fabric and the nylon-6 fabric treated with 40% FR, 2.6% DMDHEU and 4.8% TMM and cured at 165 °C for 2 min

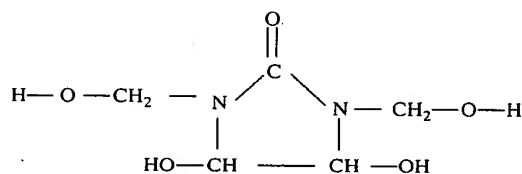
Sample description	DTG peak (°C)	DSC endothermal peak (°C)	TG solid residual at 500 °C (%)
Untreated nylon-6 fabric	424	425	10
Treated nylon-6 fabric before laundering	343	342	23
Treated nylon-6 fabric subjected to three laundering cycles	395	397	15



Scheme 2. The FR/TMM polymeric network.

with every terminal amine group in the nylon-6,6 fiber through DMDHEU/TMM and also assuming that $x = 1$ in Scheme 1, the maximum phosphorus concentration on the nylon-6,6 fiber is 0.23% (w/w). Considering the facts that the penetration of FR into the nylon fiber is poor and that the efficiency of bonding FR to cotton cellulose is approximately 60% when DMDHEU or TMM are used as the binders, the concentration of the phosphorus bound to the nylon fiber through the terminal amine groups should be far less than the maximum value of 0.23%. The data presented above show that the initial phosphorus concentration before wash on the nylon-6 fabric (4.51%) was 1.8 times that on the nylon-6,6 fabric (3.63%). The percent phosphorus retention after three laundering cycles remained the same (41%–42%) for those two fabrics. Therefore, the amount of FR bound to the nylon fabrics through the terminal amine groups of nylon is probably insignificant. We can conclude that the laundering durability of the FR on the nylon fabrics is mainly attributed to the formation of crosslinked polymeric network shown in Scheme 2. FR on the nylon fibers became a part of the crosslinked polymeric network, thus becoming durable to multiple laundering cycles.

In our previous research, we also found that the two hemiacetal groups originated from glyoxal in a DMDHEU molecule (Scheme 3) are far less reactive than those of formaldehyde. Consequently, DMDHEU



Scheme 3. DMDHEU.

mainly functions as a bifunctional reagent and reacts with FR to form a linear condensation product.

The cotton/nylon BDU fabric was treated with 40% FR in combination with DMDHEU/TMM and with XMM/TMM, as shown in Table 4, and cured at 165 °C for 2 min. The fabric thus treated was subjected to different numbers of home laundering cycles. The phosphorus concentration and the percent phosphorus retention of the treated fabric are shown in Table 5 and Fig. 4, respectively. The phosphorus concentrations (before laundering) on the fabric treated with FR/DMDHEU/TMM and FR/XMM/TMM were 3.93% and 3.89%, respectively. It decreased to 2.47% and 2.18% for the fabric treated with FR/XMM/TMM and FR/DMDHEU/TMM, respectively, after one laundering cycle, which represented 63% and 55% retention of FR on the fabric (Fig. 4). As the number of laundering cycle increased to 40, the phosphorus retention decreased to 36% and 25% for the fabric treated using XMM/TMM and DMDHEU/TMM as the binders, respectively (Fig. 4). Thus, the data presented here demonstrate that the phosphorus retention of the fabric treated with FR/XMM/TMM is notably higher than that treated with FR/DMDHEU/TMM, and the difference became more significant as the number of laundering cycle increased.

The two formulas contained the same concentration of FR and TMM. The only difference was the second

Table 4
The formulas (A1–A2) used for the treatment of cotton/nylon blend fabric

Sample code	FR (%)	DMDHEU (%)	XMM (%)	TMM (%)	Catalyst (%)	Wetting agent (%)	Wet pick-up (%)
A1	40	3.5	—	4.8	0.2	0.2	78
A2	40	—	3.4	4.8	0.2	0.2	80

Table 5

The phosphorus concentration (%) of the cotton/nylon blend (50/50) treated 40% FR and different binders, and cured at 165 °C for 2 min

Sample code	Binding system	Number of home laundering cycles				
		0	1	10	20	40
A1	3.5% DMDHEU,	3.93	2.18	1.59	1.18	0.97
	4.8% TMM					
A2	3.4% XMM,	3.89	2.47	1.99	1.65	1.39
	4.8% TMM					

bonding agent in the formulas. The fabric treated with DMDHEU/TMM as the binders showed significantly lower phosphorus retention throughout the 40 laundering cycles than that treated with XMM/TMM (Fig. 4). Thus, the data presented clearly indicate that XMM is a more effective bonding agent for FR on the cotton/nylon blend, and the FR bound to the fabric using XMM/TMM as the bonding agents is more durable to home laundering than that using DMDHEU/TMM.

The different effectiveness as a binder between XMM and DMDHEU was probably related to their ability to form a crosslinked polymeric network with FR on the fabric. Since XMM has a higher functionality than TMM, it has higher reactivity towards FR to form a crosslinked network than TMM. The higher laundering durability of the fabric treated using XMM/TMM as the binders can be attributed to the increased amount of the crosslinked network formed on the fabric. DMDHEU, on the other hand, forms linear structures with FR, as discussed previously. We found that the fabric treated with XMM/TMM showed higher stiffness than that treated with DMDHEU/TMM, which was an indication that the amount of the crosslinked network was increased on the cotton/nylon blend as the DMDHEU was replaced by XMM in the formula. The change of nylon fabric stiffness with different bonding agents in the flame retardant finishing systems will be discussed in a subsequent paper.

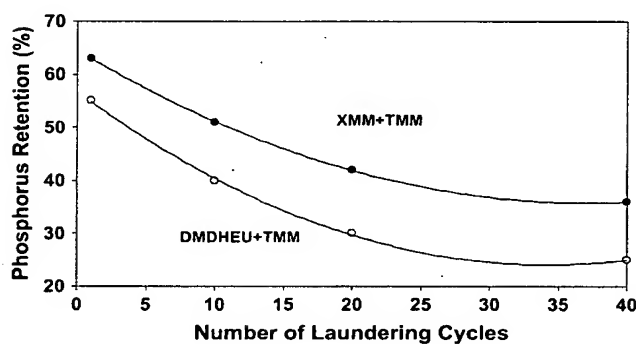


Fig. 4. The percent phosphorus retention of the nylon/cotton (50/50) blend fabric treated with 40% FR in combination with DMDHEU/TMM and XMM/TMM as a function of the number of home laundering cycles.

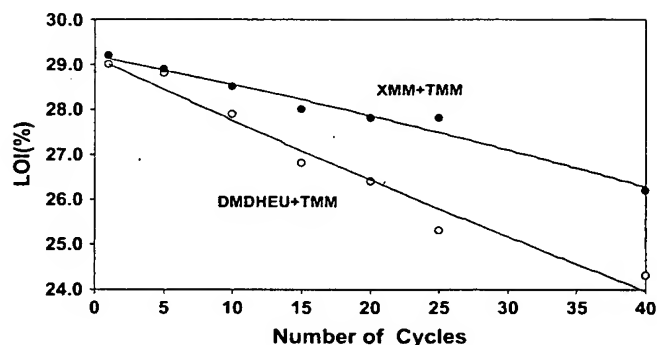


Fig. 5. The LOI (%) of the nylon/cotton (50/50) blend fabric treated with 40% FR in combination with DMDHEU/TMM and with TMM/XMM as a function of the number of home laundering cycles.

The LOI (%) of the cotton/nylon fabric treated with the two formulas is plotted against the number of laundering cycles in Fig. 5. One observes that as the number of laundering cycle increased, the LOI of the fabric treated with XMM/TMM became significantly higher than that treated with DMDHEU/TMM (Fig. 5), thus conforming that the fabric treated with XMM/TMM had higher laundering durability than that treated with DMDHEU/TMM. The difference in LOI between those two treated fabric samples became more overwhelming as the number of laundering cycle increased (Fig. 4).

We also investigated the performance of the FR-based flame retardant finishing system using different concentrations of FR, TMM and XMM, two different formulas containing FR at two concentration levels (32% and 40%), 3.4% XMM, and TMM at two concentration levels (5.1% and 2.6%) (Table 6). The treated fabric samples were cured at 165 °C for 2 min. The phosphorus concentration on the fabric treated with 40% FR, 3.4% XMM and 2.6% TMM (Sample B1) is compared with that treated with 32% FR, 3.4% XMM and 5.1% TMM (Sample B2) in Table 7, and the percent phosphorus retention of the fabric samples thus treated is plotted against the number of home laundering cycles in Fig. 5. The initial phosphorus concentration for fabric Sample B1 (3.79%) was significantly higher than that of Sample B2 (3.09%), because Sample B1 was treated with 40% FR whereas Sample B2 was treated with 32% FR (Table 6). After one laundering

Table 6

The formulas (B1–B2) used for the treatment of cotton/nylon blend fabric

Sample code	FR (%)	XMM (%)	TMM (%)	Catalyst (%)	Wetting agent (%)	Wet pick-up (%)
B1	40	3.4	2.6	0.2	0.2	78
B2	32	3.4	5.1	0.2	0.2	77

Table 7

The phosphorus concentration (%) of the cotton/nylon blend treated with the formulas B1–B2 and cured at 165 °C for 2 min

Sample code	FR concentration (%)	Number of home laundering cycles					
		0	1	10	20	40	50
B1	40	3.79	2.26	1.15	1.28	0.96	—
B2	32	3.09	2.17	1.91	1.89	1.50	1.43

cycle, Sample B2 showed higher phosphorus retention (70%) than that of Sample B1 (60%) even though its phosphorus concentration (2.17%) is slightly lower than that of Sample B1 (2.26%). When the number of the home launderings increased to 10, the phosphorus concentration of Sample B2 (1.91%) becomes notably higher than that of Sample B1 (1.55%) with corresponding phosphorus retention at 62% and 41%. The difference in percent phosphorus retention for the two treated fabric samples became more profound as the number of laundering cycle increased further. After 20 laundering cycles, Sample B2 showed 61% retention of the applied FR whereas Sample B1 had only 34% retention (Fig. 6). Thus, the data indicate that the combination of 3.4% XMM and 5.1% TMM as the binders in the system provided significantly higher retention of the FR on the fabric and also improved laundering durability.

The LOI and char length of the two treated fabric samples are presented in Tables 8 and 9, respectively. Fabric Sample B2 had LOI (29.5%) slightly higher than that of Sample B1 (29.3%) before wash even though its phosphorus content (3.09%) was lower than that of Sample B1 (3.79%). This was because the TMM concentration for Sample B2 (5.1%) is significantly higher than that of Sample B1 (2.6%). Since TMM functions as a nitrogen provider to enhance the flame retarding performance by means of phosphorus–nitrogen synergism [18–20], a higher TMM concentration in formula B2 raised the LOI of the treated fabric sample.

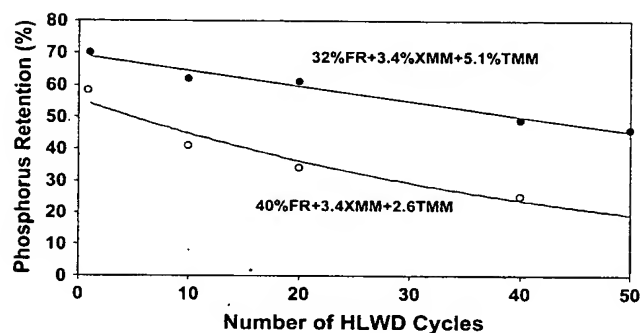


Fig. 6. The percent phosphorus retention of the nylon/cotton (50/50) blend fabric treated with FR and different melamine–formaldehyde bonding agents as a function of the number of home laundering cycles.

Table 8

The LOI (%) of the cotton/nylon blend treated with the formulas B1–B2 and cured at 165 °C for 2 min

Sample code	FR concentration (%)	Number of home laundering cycles					
		0	1	10	20	40	50
B1	40	29.3	28.4	27.2	26.1	24.5	—
B2	32	29.5	28.6	28.0	28.1	26.9	26.0

During the entire 50 home laundering cycles, Sample B2 maintained higher LOI than Sample B1, as shown in Table 8, in spite of the lower FR concentration in its formula. Fabric Sample B2 passed the vertical flammability test with a char length of 9.6 cm after 50 laundering cycles whereas Sample B1 failed the test after 40 laundering cycles (Table 9). Therefore, the fabric treated with 32% FR, 3.4% XMM and 5.1% TMM demonstrated notably better flame retarding performance and laundering durability than that treated with 40% FR, 3.4% XMM and 2.6% TMM.

In our previous research on the FR/TMM system, we found that the formation of a crosslinked network takes place only in certain FR/TMM weight ratio range [20]. The higher retention of the flame retarding agent on fabric and the better flame retarding performance after multiple laundering cycles for the fabric with a lower concentration of FR and higher concentration of the binding agents indicate that the FR-to-binder ratio in a formula plays a critical role in determining the performance of this flame retarding system.

4. Conclusions

The FR applied to the nylon-6,6 and nylon-6 fabrics becomes durable to home laundering when a bonding system including DMDHEU and TMM is present. The laundering durability of FR is probably attributed to the formation of a FR/TMM crosslinked polymeric network on the nylon fabrics.

The cotton/nylon BDU fabric treated with the combination of TMM and XMM shows high levels of flame retarding performance and laundering durability. The selection of the binders and the binders-to-FR weight ratio in a finish formulation are the two most critical parameters for achieving higher levels of flame retarding performance.

Table 9

The char length (cm) of the cotton/nylon blend treated with formulas B1–B2 and cured at 165 °C for 2 min

Sample code	FR concentration (%)	Number of home laundering cycles					
		0	1	10	20	40	50
B1	40	5.0	8.4	7.8	5.8	> 30	> 30
B2	32	5.8	6.5	9.3	6.8	8.2	9.6

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References

- [1] Lewin M. In: Lewin M, Sello SB, editors. *Handbook of fiber science and technology: chemical processing of fibers and fabrics*, vol. 2. New York: Marcel Dekker; 1984. Part B. 117 pp.
- [2] Horrocks AR. Flame-retardant finishing of textile. *Rev Prog Color* 1986;16:62.
- [3] Horrocks AR. In: Heywood D, editor. *Textile finishing*. West Yorkshire, U.K.: Society of Dyers and Colourists; 2003. 214 pp.
- [4] Levchik SV, Weil ED. Combustion and fire retardancy of aliphatic nylons. *Polym Int* 2000;49:1033.
- [5] Weil ED, Levchik SV. Current practice and recent commercial developments in flame retardancy of polyamides. *J Fire Sci* 2004;24:251.
- [6] Busch CW. US Patent, 3,639,232; 1972.
- [7] Nemes JJ, Polansky R, Herbes WF. US Patent, 3,308,098; 1967.
- [8] Bryan RJ. US Patent, 3,637,552; 1972.
- [9] Burnell MR. US Patent, 2,953,480; 1960.
- [10] Lewin M. The system polyamide/sulfamate/dipentaerythritol: flame retardancy and chemical reactions. *Polym Adv Tech* 2002;13:1091.
- [11] John HH. Flame-resistant nylon/cotton fabric and process for production thereof. US Patent, 4,812,144; 1989.
- [12] Hauser PJ. US Patent, 4,732,789; 1988.
- [13] Fleming GR, Green JR. Long wear life flame-retardant cotton blend fabrics. US Patent, 5,468,545; 1995.
- [14] Hansen JH. Flame-resistant nylon/cotton fabrics. US Patent, 4,750,911; 1988.
- [15] Fleming GR, Green JR. Long wear life flame-retardant cotton blend fabrics. US Patent, 5,480,458; 1996.
- [16] Cole R. Process for the flame-resistant treatment of textiles. US Patent, 5,942,006; 1999.
- [17] Yang CQ, Wu W. Combination of a hydroxyl-functional organophosphorus oligomer and a multifunctional carboxylic acid as a flame retardant finishing system for cotton: part I. The chemical reactions. *Fire Mater* 2003;27:223.
- [18] Yang CQ, Wu W. Combination of a hydroxyl-functional organophosphorus oligomer and a multifunctional carboxylic acid as a flame retardant finishing system for cotton: part II. Formation of calcium salt during laundering. *Fire Mater* 2003;27:239.
- [19] Wu W, Yang CQ. Comparison of DMDHEU and melamine formaldehyde as the binding system for a hydroxy-functional organophosphorus flame retarding agent on cotton. *J Fire Sci* 2004;22:125.
- [20] Wu W, Yang CQ. Statistical analysis of the performance of the flame retardant finishing system consisting of a hydroxy-functional organophosphorus oligomer and the mixture of DMDHEU and melamine formaldehyde resin. *Polym Degrad Stab* 2004;85:623.
- [21] Yang CQ, Wu W. The combination of a hydroxy-functional organophosphorus oligomer and melamine-formaldehyde as a flame retarding finishing system for cotton. *Fire Mater*, in press. Available from: www3.interscience.wiley.com.
- [22] Hornsby PR, Wang J, Rothon R. Thermal decomposition behaviour of polyamide fire-retardant compositions containing magnesium hydroxide filler. *Polym Degrad Stab* 1996;51:235.
- [23] Levchik SV, Weil ED, Lewin M. Thermal decomposition of aliphatic nylons. *Polym Int* 1999;48:532.
- [24] Horrocks AR, Zhang S. Char formation in polyamide (nylon 6 and nylon 6.6) and wool keratin phosphorylated by polyol chlorides. *Textile Res J* 2004;74:433.